

Stationary Inverted Lyman Population Formed from Incandescently Heated Hydrogen Gas with Certain Catalysts

R. Mills, P. Ray
BlackLight Power, Inc.
493 Old Trenton Road
Cranbury, NJ 08512

ABSTRACT

Rb^+ to Rb^{2+} and $2K^+$ to $K+K^{2+}$ each provide a reaction with a net enthalpy equal to the potential energy of atomic hydrogen. The presence of these gaseous ions with thermally dissociated hydrogen formed a plasma having strong VUV emission with a stationary inverted Lyman population. We propose an energetic catalytic reaction involving a resonance energy transfer between hydrogen atoms and Rb^+ or $2K^+$ to form a very stable novel hydride ion. Its predicted binding energy of 3.0468 eV with the fine structure was observed at 4071 \AA , and its predicted bound-free hyperfine structure lines $E_{HF} = j^2 3.00213 \times 10^{-5} + 3.0563\text{ eV}$ (j is an integer) matched those observed for $j=1$ to $j=37$ to within a 1 part per 10^5 . This catalytic reaction may pump a cw HI laser.

1. Introduction

The Lyman α , β , and γ lines of atomic hydrogen at 121.6 nm, 102.6 nm, and 97.3 nm in the vacuum ultraviolet (VUV) region are due to the transitions from $n=2$, $n=3$, and $n=4$ to $n=1$, respectively. These lines are of great importance in many applications ranging from photochemistry, to laboratory simulations of planetary atmospheres, to astrophysics and plasma physics. In plasma physics, the Lyman series line intensities and their ratios are frequently used in the determination of plasma parameters such as hydrogen number densities and other quantities such as particle fluxes or ion recombination processes [1-2]. For the last four decades, scientist from academia and industry have been searching for lasers using hydrogen plasma [3-6]. Developed sources that provide a usefully intense hydrogen plasma are high powered lasers, arcs and high voltage DC and RF discharges, synchrotron devices, inductively coupled plasma generators, and magnetically confined plasmas. However, the generation of population inversion is very difficult. Recombining expanding plasmas jets formed by methods such as arcs or pulsed discharges is considered one of the most promising methods of realizing an HI laser.

It was reported previously that a new plasma source has been developed that operates by incandescently heating a hydrogen dissociator to provide atomic hydrogen and heats a catalyst such that it becomes gaseous and reacts with the atomic hydrogen to produce a plasma called a resonance transfer or rt-plasma. It was extraordinary, that intense VUV emission was observed by Mills et al. [7-8] at low temperatures (e.g. $\approx 10^3$ K) and an extraordinary low field strength of about 1-2 V/cm from atomic hydrogen and certain atomized elements or certain gaseous ions which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, 27.2 eV.

The theory given previously [9-11] is based on applying Maxwell's equations to the Schrödinger equation. The familiar Rydberg equation (Eq. (1)) arises for the hydrogen excited states for $n > 1$ of Eq. (2).

$$E_n = -\frac{e^2}{n^2 8\pi\epsilon_0 a_H} = -\frac{13.598 \text{ eV}}{n^2} \quad (1)$$

$$n = 1, 2, 3, \dots \quad (2)$$

An additional result is that atomic hydrogen may undergo a catalytic reaction with certain atoms and ions which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, $m \cdot 27.2 \text{ eV}$ wherein m is an integer. The reaction involves a nonradiative energy transfer to form a hydrogen atom that is lower in energy than unreacted atomic hydrogen that corresponds to a fractional principal quantum number. That is

$$n = \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots, \frac{1}{p}; \quad p \text{ is an integer} \quad (3)$$

replaces the well known parameter $n = \text{integer}$ in the Rydberg equation for hydrogen excited states. The $n=1$ state of hydrogen and the $n = \frac{1}{\text{integer}}$ states of hydrogen are nonradiative, but a transition between two nonradiative states, say $n=1$ to $n=1/2$, is possible via a nonradiative energy transfer. Thus, a catalyst provides a net positive enthalpy of reaction of $m \cdot 27.2 \text{ eV}$ (i.e. it resonantly accepts the nonradiative energy transfer from hydrogen atoms and releases the energy to the surroundings to affect electronic transitions to fractional quantum energy levels). As a consequence of the nonradiative energy transfer, the hydrogen atom becomes unstable and emits further energy until it achieves a lower-energy nonradiative state having a principal energy level given by Eqs. (1) and (3). Processes such as hydrogen molecular bond formation that occur without photons and that require collisions are common [12]. Also, some commercial phosphors are based on resonant nonradiative energy transfer involving multipole coupling [13].

The second ionization energy of potassium is 31.63 eV , and K^+ releases 4.34 eV when it is reduced to K . The combination of reactions K^+ to K^{2+} and K^+ to K , then, has a net enthalpy of reaction of 27.28 eV . Also, the second ionization energy of rubidium is 27.28 eV ; thus, the reaction Rb^+ to Rb^{2+} has a net enthalpy of reaction of 27.28 eV . The catalyst product $H(1/2)$ is predicted to be a highly reactive intermediate which further reacts to form a novel hydride ion $H^-(1/2)$. In this Letter, we report that the population of the level $n=2$ of hydrogen was continuously inverted with respect to $n=3$ and $n=4$ in an rt-plasma formed with K^+ and Rb^+ catalysts. To our knowledge, this is the first report of population inversion in a chemically generated plasma. The plasma was further

characterized by measuring the electron temperature T_e from intensity ratios of alkali lines, the ion temperature and number density from Balmer α line broadening, and the hydride ion product of catalysis by high resolution visible spectroscopy.

2. Experimental

The VUV spectrum (900–1300 Å), the width of the 6563 Å Balmer α line, and the high resolution visible spectrum were recorded on light emitted from a hydrogen microwave discharge performed according to methods reported previously [14] that served as a control for measurements recorded on light emitted from rt-plasmas of hydrogen with KNO_3 or $RbNO_3$. The experimental set up described previously [7-8] comprised a thermally insulated quartz cell with a cap that incorporated ports for gas inlet, outlet, and photon detection. A tungsten filament heater and hydrogen dissociator were in the quartz tube as well as a cylindrical titanium screen that served as a second hydrogen dissociator that was coated with catalysts KNO_3 or $RbNO_3$ and control materials $Mg(NO_3)_2$ or $Al(NO_3)_3$. The cell was maintained at 50 °C for four hours with helium flowing at 30 sccm at a pressure of 0.1 Torr. The cell was then operated with and without an ultrapure hydrogen flow rate of 5.5 sccm maintained at 300 mTorr. The titanium screen was electrically floated with 250 W of power applied to the filament. The temperature of the tungsten filament was estimated to be in the range 1100 to 1500 °C. The external cell wall temperature was about 700 °C.

The VUV spectrometer was a normal incidence 0.2 meter monochromator equipped with a 1200 lines/mm holographic grating with a platinum coating that covered the region 20–5600 Å. The VUV spectrum was recorded with a CEM. The wavelength resolution was about 0.2 Å (FWHM) with slit widths of 50 μm . The increment was 2 Å and the dwell time was 500 ms. The VUV spectrum (900–1300 Å) of the rt-plasma cell emission was recorded at about the point of the maximum Lyman α emission to confirm the rt-plasma before the line broadening and high resolution visible spectrum in the region of 4070 Å were recorded. In addition, the visible spectrum 4000–5600 Å was recorded with the normal incidence VUV spectrometer using a PMT and a sodium

salicylate scintillator to record K lines.

The electron temperature T_e of the $RbNO_3$ and KNO_3 cell was measured from the ratio of the intensity of the Rb^+ 741.4 Å line to that of the Rb^{2+} 815.3 Å line and the ratio of the K^+ 612.6 Å line to that of the K^{2+} 546.1 Å line, respectively, as described by Griem [15].

The plasma emission from a hydrogen microwave discharge [16] control and each rt-plasma maintained in the filament heated cell was fiber-optically coupled to a high resolution visible spectrometer capable of a resolution of ± 0.06 Å. The slits were set to $20 \mu m$, the step size was 0.1 Å, and the spectra (4000–4090 Å and 6560–6570 Å) were recorded by a PMT in a single accumulation with a 1 second integration time.

3. Results and discussion

A. Hydrogen Lyman series emission

The VUV spectra (900–1300 Å) of the cell emission recorded at about the point of the maximum Lyman α emission from the KNO_3 and $RbNO_3$ gas cell are shown in Figures 1 and 2, respectively, with the superimposed spectrum from the hydrogen microwave plasma. Strong Lyman series VUV emission was observed only with KNO_3 or $RbNO_3$ and hydrogen. The Lyman series lines of the rt-plasma showed population inversion with much greater intensity of atomic hydrogen versus molecular hydrogen compared to the microwave plasma emission. The population density of the excited hydrogen atoms N_α , N_β , and N_γ with principal quantum numbers $n=2,3$, and 4, respectively, were obtained from their intensity integrated over the spectral peaks corrected by their Einstein coefficients. The population ratios, $\frac{N_\beta}{N_\alpha}$ and $\frac{N_\gamma}{N_\alpha}$, for pure H_2 and H_2 with KNO_3 or $RbNO_3$ are given in Table 1.

The important parameter for a lasing medium is the reduced population density $\frac{N}{g}$ given by the population density N divided by the statistical weight g as discussed by Akatsuka et al. [6]. The ratio of $\frac{N}{g}$ for L_β to L_α and L_γ to L_α given in Table 2 demonstrate that with appropriate

cavity length and mirror reflection coefficient cw laser oscillations may be obtained between $n=3$ and $n=2$ since the corresponding $\frac{N_\beta g_\alpha}{N_\alpha g_\beta} > 1$ [6].

For the plasma conditions of this experiment ($T_e \approx 0.7-0.8$ eV, $n_e \approx 10^{11}$ cm $^{-3}$), a threshold reduced overpopulation of $\approx 2 \times 10^8$ cm $^{-3}$ is required for lasing assuming a cavity length of 5 cm and a mirror reflection coefficient of 0.99. Initial modeling results based on the collisional-radiative model [6] suggest that the threshold condition is achieved for these plasmas [17]. Due to the short lifetime of the Balmer α line, an exceptionally monochromatic laser with the possibility of fast switching is anticipated.

In a non-recombining plasma [6], thermal electron collisional mechanisms can not produce the conditions necessary for population inversion. All known sources of excitation were exhausted [18]. The observation, then, of population inversion indicates the presence of free energy in the system. This is further evidence that a new chemical source of energy, greater than 12 eV/atom was present. The only possibility known to the authors is the proposed reaction to form hydrogen states given by Eqs. (1) and (3).

T_e was determined to be 0.84 eV and 0.76 eV for the K^+ and Rb^+ rt-plasma respectively. Similarly, $k_B T_e = (0.30-0.43)$ eV was determined for a K^+ rt-plasma as reported by Conrads et al. [18] with the assumption of a Maxwell Boltzmann distribution of the level population, and a slightly higher temperature of $k_B T_e = (0.32-0.48)$ eV was found when a corona model was applied. The data indicated that the electron temperature was not higher than $k_B T_e = 0.5$ eV. On this basis, it was astonishing that a strong Lyman beta transition appeared in the spectra since an excitation energy of 12.1 eV is required. This energy is a factor of about 25 above the measured thermal energy. The amount of electrons in the Maxwell tail that had enough energy to enhance the Lyman transition was 11 orders of magnitude lower than the total number of electrons. Longer range fields (of the order of mm) were only about a 1 V/cm. In addition to electron collisional excitation, known chemical reactions, resonant photon transfer, and multiphoton absorption, and the lowering of the ionization and excitation energies by the state of "non ideality" in dense plasmas were also rejected as the source of ionization or excitation to form the hydrogen plasma.

A source of energy other than that provided by the electric field or known chemical reactions must be considered. We propose that the plasma formed chemically rather than electrically and that the product of the energetic chemical reaction of atomic hydrogen with potassium or rubidium ions which serve as catalysts as well as reactants are compounds having hydride ions $H^-(1/p)$; p =integer discussed in Section 3C. Prior related studies that support the possibility of a novel reaction of atomic hydrogen which produces a chemically generated or assisted plasma (rt-plasma) and produces novel hydride compounds include VUV spectroscopy [7-8, 14, 16, 18-27], characteristic emission from catalysts and the hydride ion products [22-25], lower-energy hydrogen emission [14, 19, 21], chemically formed plasmas [7-8, 17-18, 22-27], Balmer α line broadening [16-17, 19, 25, 28], elevated electron temperature [16-17, 19], anomalous plasma afterglow duration [27], power generation [26, 28-29], and analysis of novel chemical compounds [30].

The lines of K^+ , and K^{2+} corresponding to the catalytic reaction were observed as reported previously [23] with the assignments confirmed by a standard potassium plasma spectrum and NIST tables [31-32]. K^{2+} was observed at 510 Å and 550 Å, and K^+ was observed at 620 Å. K was observed at 3447 Å, 4965 Å, and 5084 Å.

The lines of Rb^+ and Rb^{2+} corresponding to the catalytic reaction were observed as reported previously [24] with the assignments confirmed by the NIST tables [32]. Line emission corresponding to Rb^{2+} was observed at 815.9 Å, 591 Å, 581 Å, 556 Å, and 533 Å. Rb^+ was observed at 741.5 Å, 711 Å, 697 Å, and 643.8 Å.

Then the inverted population is explained by a resonance nonradiative energy transfer from the short-lived highly energetic intermediates¹, atoms undergoing catalyzed transitions to states given by

¹ As a consequence of the nonradiative energy transfer of $m \cdot 27.2 \text{ eV}$ to the catalyst, the hydrogen atom becomes unstable and emits further energy until it achieves a lower-energy nonradiative state having a principal energy level given by Eqs. (1) and (3). Thus, these intermediate states also correspond to an inverted population, and the emission from these states with energies of $q \cdot 13.6 \text{ eV}$ where $q=1,2,3,4,6,7,8,9,11,12$ shown in Refs. 14 and 19 may be the basis of a laser in the EUV and soft X-ray, since the excitation of the corresponding relaxed Rydberg state atoms $H(1/(p+m))$ requires the participation of a nonradiative process [18].

Eqs. (1) and (3), to yield $H(n>2)$ atoms directly by multipole coupling [19] and fast $H(n=1)$ atoms. The emission of $H(n=3)$ from fast $H(n=1)$ atoms excited by collisions with the background H_2 has been discussed by Radovanov et al. [33]. Formation of H^+ is also predicted which is far from thermal equilibrium in terms of the ion temperature as discussed in Section 3B. Akatsuka et al. [6] show that it is characteristic of cold recombining plasmas to have the high lying levels in local thermodynamic equilibrium (LTE); whereas, for the low lying levels, population inversion is obtained when T_e becomes low with an appropriate electron density as shown by the Saha-Boltzmann equation.

B. Measurement of hydrogen ion temperature and number density from Balmer line broadening

The method of Videnovic et al. [34] was used to calculate the energetic hydrogen atom densities and energies from the width of the 6563 Å Balmer α line emitted from microwave and rt-plasmas. The full half-width $\Delta\lambda_G$ of each Gaussian results from the Doppler ($\Delta\lambda_D$) and instrumental ($\Delta\lambda_I$) half-widths:

$$\Delta\lambda_G = \sqrt{\Delta\lambda_D^2 + \Delta\lambda_I^2} \quad (4)$$

$\Delta\lambda_I$ in our experiments was 0.06 Å. The temperature was calculated from the Doppler half-width using the formula:

$$\Delta\lambda_D = 7.16 \times 10^{-6} \lambda_0 \left(\frac{T}{\mu} \right)^{1/2} (\text{Å}) \quad (5)$$

where λ_0 is the line wavelength in Å, T is the temperature in K ($1 \text{ eV} = 11,605 \text{ K}$), and μ is the molecular weight ($=1$ for hydrogen). In each case; the average Doppler half-width that was not appreciably changed with pressure varied by $\pm 5\%$ corresponding to an error in the energy of $\pm 5\%$. The corresponding number densities for noble gas-hydrogen mixtures varied by $\pm 20\%$ depending on the pressure.

The results of the 6563 Å Balmer α line width measured with the high resolution ($\pm 0.06 \text{ Å}$) visible spectrometer on light emitted from rt-plasmas of hydrogen with KNO_3 is shown in Figures 3. Significant line broadening of 17 and 9 eV and an atom density of 4×10^{11} and $6 \times 10^{11} \text{ atoms/cm}^3$ were observed from an rt-plasma of hydrogen

formed with K^+ and Rb^+ , respectively. A hydrogen microwave plasma maintained at the same total pressure showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 3\text{ eV}$ and a density of $2 \times 10^{11} \text{ atoms/cm}^3$. These results could not be explained by Stark or thermal broadening or electric field acceleration of charged species since the measured field of the incandescent heater was extremely weak, 1 V/cm, corresponding to a broadening of much less than 1 eV.

C. High resolution visible spectroscopy recorded on rt-plasmas

The catalyst product $H(1/2)$ was predicted to be a highly reactive intermediate which further reacts to form a novel hydride ion $H^-(1/2)$ with a predicted binding energy of 3.0468 eV given by the following formula [9, 25] for the hydride binding energies E_B :

$$E_B = \frac{\hbar^2 \sqrt{s(s+1)}}{8\mu_e a_0^2 \left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^2} - \frac{\pi\mu_0 e^2 \hbar^2}{m_e^2 a_0^3} \left(1 + \frac{2^2}{\left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^3} \right) \quad (6)$$

where p is an integer greater than one (1/2 in this case), $s=1/2$, \hbar is Planck's constant bar, μ_0 is the permeability of vacuum, m_e is the mass of the electron, μ_e is the reduced electron mass, a_0 is the Bohr radius, and e is the elementary charge. The ionic radius is

$$r_i = \frac{a_0}{p} \left(1 + \sqrt{s(s+1)} \right); s = \frac{1}{2} \quad (7)$$

For both the KNO_3 and $RbNO_3$ -rt plasma, this hydride ion was observed with the fine structure transition by high resolution visible spectroscopy as a broad peak at 4071 Å with a FWHM of 1.2 Å as shown in Figure 4 for $RbNO_3$. From the electron g factor, bound-free hyperfine structure lines of $H^-(1/2)$ were predicted with energies E_{HF} given by the sum of the binding energy peak E_B^* (Eqs. (6) and (7) with the fine structure), the spin-pairing energy E_{sp} , and the fluxon energy E_ϕ that was derived previously [25].

$$\begin{aligned} E_{HF} &= E_\phi + E_{sp} + E_B^* = j^2 2(g-2) \frac{\mu_B}{\sqrt{s(s+1)}} \frac{\mu_0}{r^3} \left(\frac{e\hbar}{2m_e} \right) + g \frac{\mu_0}{r^3} \left(\frac{e\hbar}{2m_e} \right)^2 + E_B^* \\ &= j^2 3.00213 \times 10^{-5} + 3.0563 \text{ eV} \end{aligned} \quad (8)$$

where j is an integer. The predicted spectrum is an inverse Rydberg-type series that converges at increasing wavelengths and terminates at 3.0563 eV —the hydride binding energy with the fine structure plus the spin-pairing energy. The high resolution visible plasma emission spectra in the region of 4000 \AA to 4060 \AA show in Figure 4 matched the predicted emission lines for $j=1$ to $j=37$ to 1 part in 10^5 as shown in Figure 5.

4. Conclusion

Rb^+ to Rb^{2+} and $2K^+$ to $K+K^{2+}$ each provide a reaction with a net enthalpy equal to the potential energy of atomic hydrogen, 27.2 eV . The presence of these gaseous ions with thermally dissociated hydrogen formed a plasma having strong VUV emission with an inverted Lyman population. We propose an energetic catalytic reaction involving a resonance energy transfer between hydrogen atoms and Rb^+ or $2K^+$ to form Rb^{2+} and $K+K^{2+}$, respectively, and a hydrogen atom with a Rydberg state $n=1/2$. Emission from Rb^+ , Rb^{2+} and K , K^+ , and K^{2+} were observed. The catalyst product $H(1/2)$ was predicted to be a highly reactive intermediate which further reacts to form a novel hydride ion $H^-(1/2)$. Its predicted binding energy of 3.0468 eV with the fine structure was observed at 4071 \AA with its predicted bound-free hyperfine structure lines $E_{HF} = j^2 3.00213 \times 10^{-5} + 3.0563\text{ eV}$ (j is an integer) that matched for $j=1$ to $j=37$ to within a 1 part per 10^5 .

The ionization and population of excited atomic hydrogen levels was attributed to energy provided by atoms undergoing catalyzed transitions to states given by Eqs. (1) and (3). The high ion temperature with a relatively low electron temperature, $T_e < 1\text{ eV}$, were characteristic of cold recombining plasmas [6]. These conditions of the rt-plasmas favored an inverted population in the lower levels. Thus, the catalysis of atomic hydrogen may pump a cw HI laser. From our results, laser oscillations are expected between $n=3$ and $n=2$.

References

- [1] C. Zimmermann, R. Kallenbach, T. W. Hansch, Phys. Rev. Lett., Vol. 65, (1990), p. 571.

- [2] T. Ibuki, Chem. Phys. Lett., Vol. 94, (1990), p. 169.
- [3] L. I. Gudzenko, L. A. Shelepin, Sov. Phys. JEPT, Vol. 18, (1963), p. 998.
- [4] S. Suckewer, H. Fishman, J. Appl. Phys., Vol. 51, (1980), p. 1922.
- [5] W. T. Silfvast, O. R. Wood, J. Opt. Soc. Am. B, Vol. 4, (1987), p. 609.
- [6] H. Akatsuka, M. Suzuki, Phys. Rev. E, Vol. 49, (1994), pp. 1534-1544.
- [7] R. Mills, J. Dong, Y. Lu, Int. J. Hydrogen Energy, Vol. 25, (2000), pp. 919-943.
- [8] R. Mills and M. Nansteel, P. Ray, IEEE Transactions on Plasma Science, in press.
- [9] R. Mills, *The Grand Unified Theory of Classical Quantum Mechanics*, September 2001 Edition, BlackLight Power, Inc., Cranbury, New Jersey, Distributed by Amazon.com; posted at www.blacklightpower.com.
- [10] R. Mills, Int. J. Hydrogen Energy, Vol. 27, No. 5, (2002), pp. 565-590.
- [11] R. Mills, Int. J. Hydrogen Energy, Vol. 26, No. 10, (2001), pp. 1059-1096.
- [12] N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Volume I, Oxford, Clarendon Press, (1950), p.17.
- [13] M. D. Lamb, *Luminescence Spectroscopy*, Academic Press, London, (1978), p. 68.
- [14] R. Mills, P. Ray, Int. J. Hydrogen Energy, Vol. 27, No. 3, pp. 301-322.
- [15] H. R. Griem, *Principle of Plasma Spectroscopy*, Cambridge University Press, (1987).
- [16] R. L. Mills, P. Ray, B. Dhandapani, J. He, Chem. Phys., submitted.
- [17] R. L. Mills, P. Ray, R. Mayo, IEEE Transactions on Plasma Science, submitted.
- [18] H. Conrads, R. Mills, Th. Wrubel, Plasma Sources Science and Technology, submitted.
- [19] R. L. Mills, P. Ray, B. Dhandapani, J. He, J. of Phys. Chem., submitted.
- [20] R. Mills, Int. J. Hydrogen Energy, Vol. 26, No. 6, (2001), pp. 579-592.
- [21] R. Mills, P. Ray, Int. J. Hydrogen Energy, Vol. 27, No. 5, (2002), pp. 533-564.
- [22] R. Mills, Int. J. Hydrogen Energy, Vol. 26, No. 10, (2001), pp. 1041-1058.
- [23] R. Mills, P. Ray, Int. J. Hydrogen Energy, Vol. 27, No. 2, (2002), pp. 183-192.
- [24] R. L. Mills, P. Ray, Int. J. Hydrogen Energy, in press.

- [25] R. L. Mills, P. Ray, *Int. J. Hydrogen Energy*, in press.
- [26] R. Mills, M. Nansteel, and Y. Lu, *Int. J. Hydrogen Energy*, Vol. 26, No. 4, (2001), pp. 309-326.
- [27] R. Mills, T. Onuma, and Y. Lu, *Int. J. Hydrogen Energy*, Vol. 26, No. 7, July, (2001), pp. 749-762.
- [28] R. Mills, A. Voigt, P. Ray, M. Nanstell, *Int. J. Hydrogen Energy*, Vol. 27, No. 6, (2002), pp. 671-685.
- [29] R. Mills, N. Greenig, S. Hicks, *Int. J. Hydrogen Energy*, Vol. 27, No. 6, (2002), pp. 651-670.
- [30] R. Mills, B. Dhandapani, M. Nansteel, J. He, T. Shannon, A. Echezuria, *Int. J. of Hydrogen Energy*, Vol. 26, No. 4, (2001), pp. 339-367.
- [31] R. Kelly, *Journal of Physical and Chemical Reference Data*, Part I (H-Cr), Volume 16, (1987), Supplement No. 1, Published by the American Chemical Society and the American Institute of Physics for the National Bureau of Standards, pp. 418-422.
- [32] NIST Atomic Spectra Database, www.physics.nist.gov/cgi-bin/AtData/display.ksh.
- [33] S. B. Radovanov, K. Dzierzega, J. R. Roberts, J. K. Olthoff, *Appl. Phys. Lett.*, Vol. 66, No. 20, (1995), pp. 2637-2639.
- [34] I. R. Videnovic, N. Konjevic, M. M. Kuraica, *Spectrochimica Acta*, Part B, Vol. 51, (1996), pp. 1707-1731.

Table 1. The population density ratios $\frac{N_\beta}{N_\alpha}$ and $\frac{N_\gamma}{N_\alpha}$ for pure H_2 , KNO_3 , and $RbNO_3$.

Plasma Gas	$\frac{N_\beta}{N_\alpha}$	$\frac{N_\gamma}{N_\alpha}$
Pure H_2 ^a	0.664	0.521
KNO_3	4.72	3.48
$RbNO_3$	4.30	1.26

^a Measured on microwave discharge maintained according to the method of ref. 14.

Table 2. The reduced population density ratios $\frac{N}{g}$ for pure H_2 , KNO_3 , and $RbNO_3$.

Plasma Gas	$\frac{N_\beta}{N_\alpha} \frac{g_\alpha}{g_\beta}$ a	$\frac{N_\gamma}{N_\alpha} \frac{g_\alpha}{g_\gamma}$ b
Pure H_2 ^c	0.292	0.130 ^c
KNO_3	2.07	0.870
$RbNO_3$	1.89	0.314

a $\frac{g_\alpha}{g_\beta} = 0.444$ where $g = 2n^2$ and n is the principal quantum number

b $\frac{g_\alpha}{g_\gamma} = 0.250$

^c Measured on microwave discharge maintained according to the method of ref. 14.

Figure Captions

Figure 1. The VUV spectra (900–1300 Å) of the cell emission from hydrogen microwave plasma (dotted line) and the KNO_3 -hydrogen rt-plasma (solid line) with an inverted Lyman population.

Figure 2. The VUV spectra (900–1300 Å) of the cell emission from hydrogen microwave plasma (dotted line) and the $RbNO_3$ -hydrogen rt-plasma (solid line) with an inverted Lyman population.

Figure 3. The 6563 Å Balmer α line width recorded with a high resolution (± 0.06 Å) visible spectrometer on a rt-plasma formed with K^+ catalyst. Significant broadening was observed corresponding to an average hydrogen atom temperature of 17 eV.

Figure 4. The high resolution visible spectrum in the region of 4000 Å to 4090 Å recorded on the emission of a rt-plasma formed with Rb^+ catalyst from vaporized $RbNO_3$. The $H^-(1/2)$ hydride ion with a predicted binding energy of 3.0468 eV with the fine structure was observed as a broad peak at 4071 Å with a FWHM of 1.2 Å. An observed inverse Rydberg-type series of broad emission lines that converged at increasing wavelengths and terminated at about 3.0563 eV—the hydride binding energy with the fine structure plus the spin-pairing energy—matched the theoretical bound-free hyperfine energies E_{HF} given by $E_{HF} = j^2 3.00213 \times 10^{-5} + 3.0563$ eV for $j=1$ to $j=37$.

Figure 5. The plot of the theoretical bound-free hyperfine air wavelengths corresponding to energies E_{HF} given by $E_{HF} = j^2 3.00213 \times 10^{-5} + 3.0563$ eV (Eq. (8)) for $j=1$ to $j=37$ and the wavelengths observed for the inverse Rydberg-type series of broad emission lines shown in Figure 4. The agreement was better than within a 1 part per 10^5 .

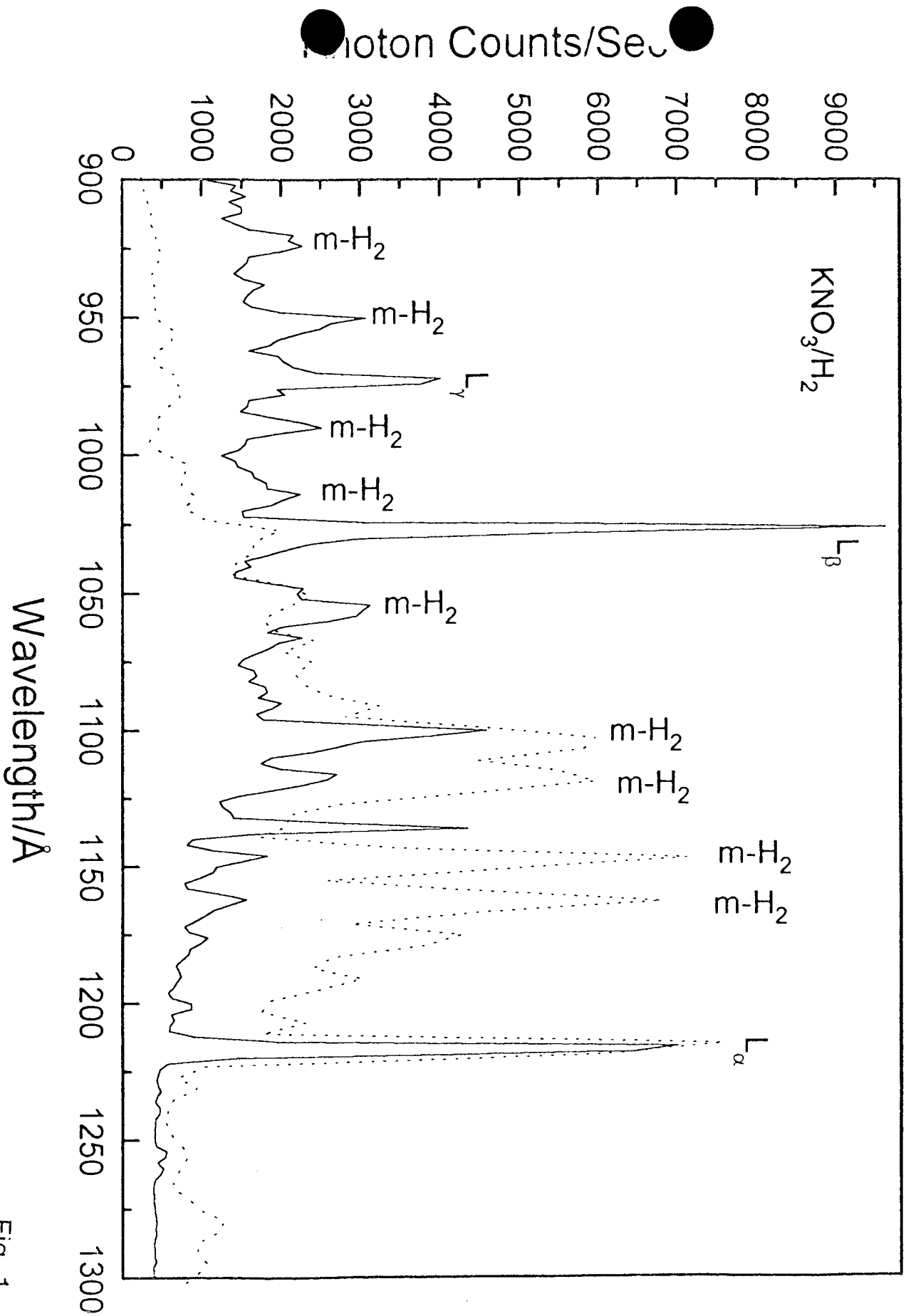


Fig. 1

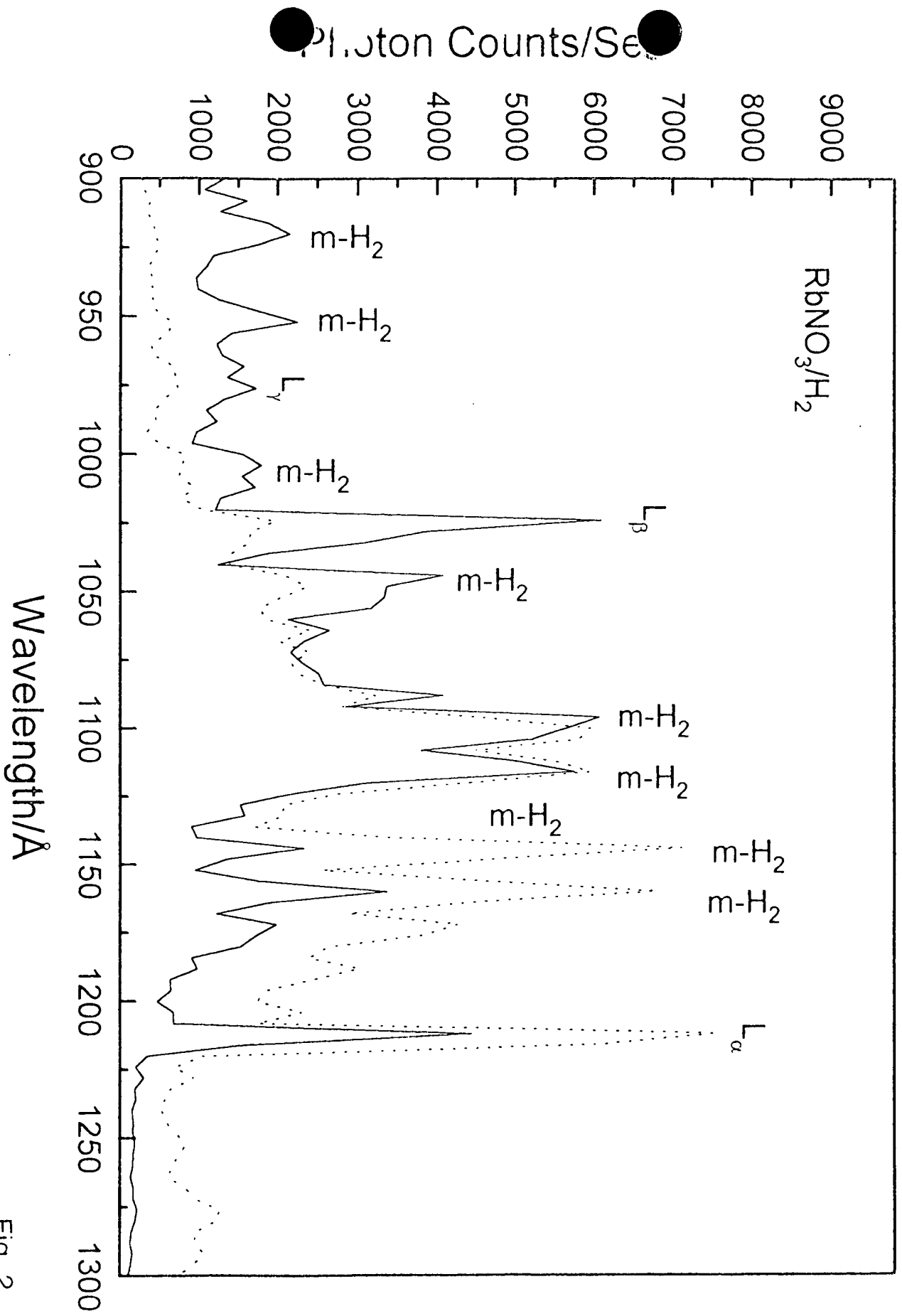


Fig. 2

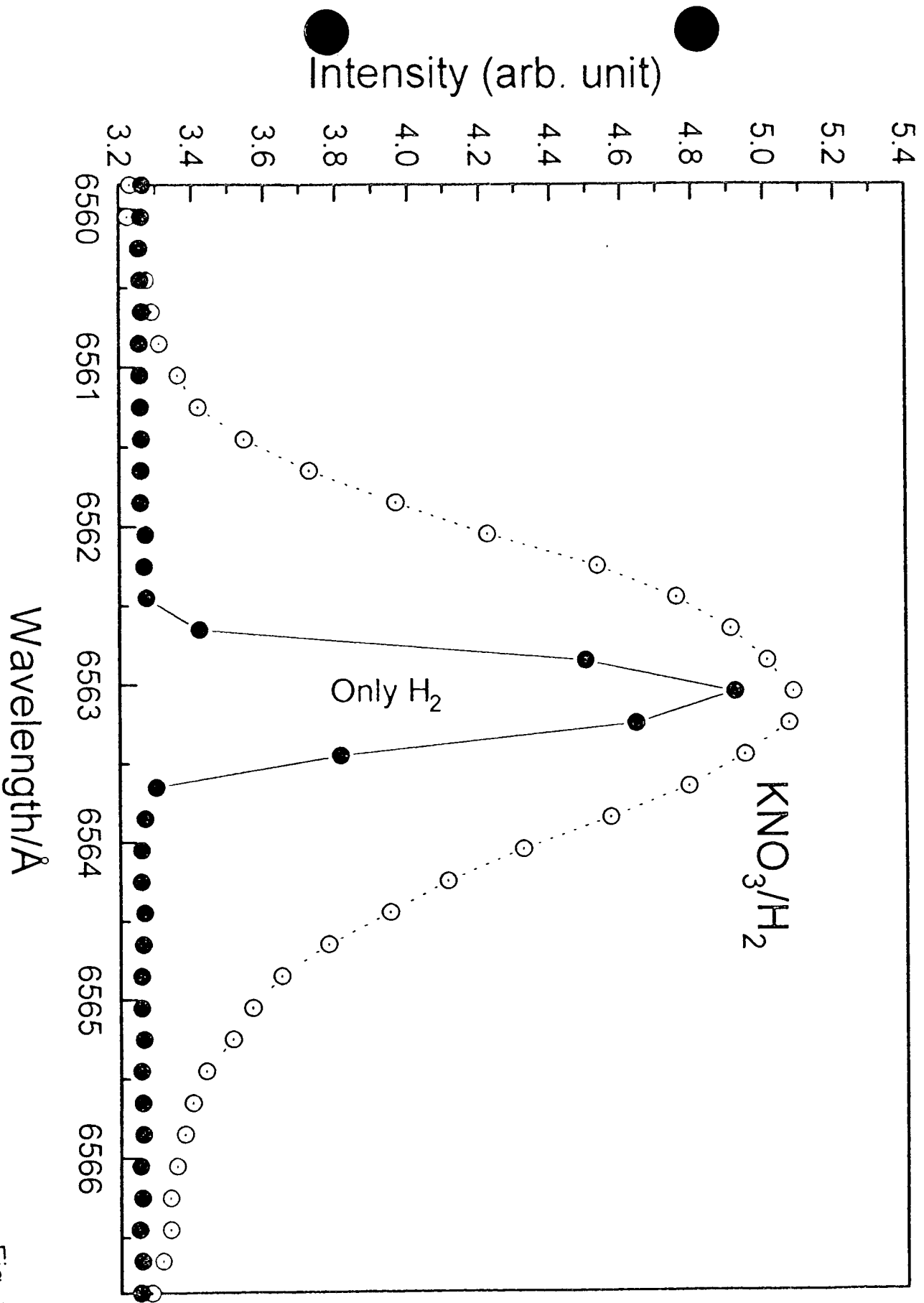


Fig. 3

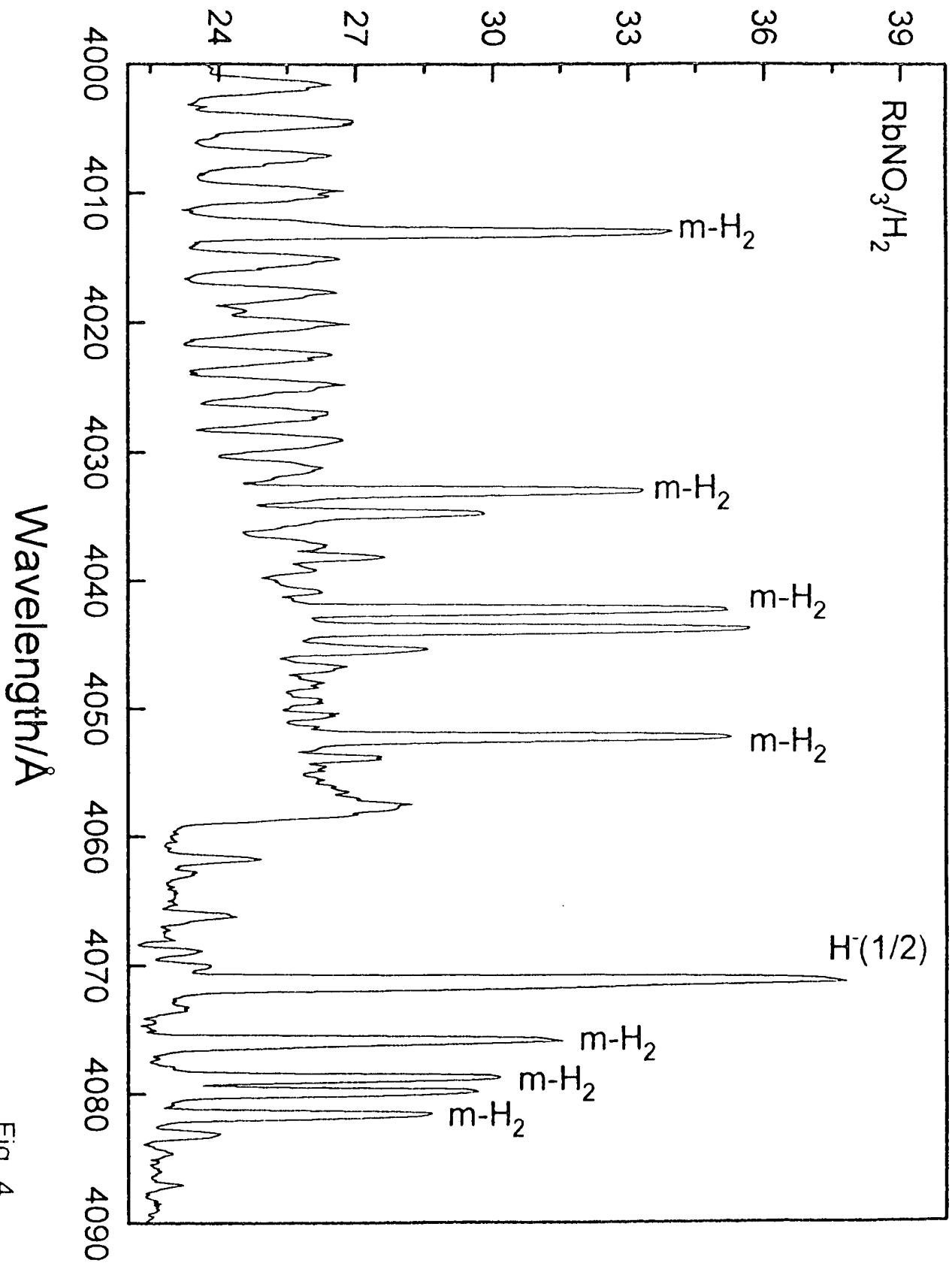


Fig. 4

Figure 5

